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(54) **Finished aramid fibers, exhibiting no deposit during processing.**

(57) An aramid fiber is disclosed having a finish of the potassium salt of ethoxylated alkyl phosphate acid esters wherein the finish permits the fiber to exhibit excellent static electricity characteristics and substantially eliminates deposits of the finish on fiber handling machinery as a result of normal handling forces. The preferred finish is the potassium salt of mono/didecyl alcohol (2EO) phosphate ester.

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ARAMID FIBERS WITH DEPOSIT-FREE FINISH

Background of the Invention

Field of the Invention

This invention relates to finishes for aramid fibers which not only increase surface lubricity and improve the static electricity characteristics of the fibers, but also do not rub off of the fibers as a result of normal handling forces. The fibers of this invention, with the prescribed finishes, exhibit little or no deposit of the finish material on fiber guides and in other areas on fibers handling machinery during processing of the fiber product.

Description of the Prior Art

Finishes have been put onto fibers almost since fibers have been made. Finishes are used to change the handling or performance characteristics of a fiber in specific ways; and finishes are often very specific in the results which are achieved on fibers of particular materials.

As an example, potassium salts of alkyl phosphate acid esters have long been used as a finish material for decreasing electrostatic charge buildup and improving the handleability of polyester and nylon fibers. Indeed, such aliphatic phosphate salts have been used with some success as antistatic finishes for aramid fibers but they have left troublesome deposits on fiber guides and other elements of the fiber handling machinery during processing of the fibers.

Fatty acid esters, such as coconut oil, castor oil, and polyethylene glycol mono/di fatty acid esters, have been commonly used as finish ingredients to improve the lubricity of aramid fibers but these ingredients don't help in reducing static charges.

Summary of the Invention

The present invention provides an aramid fiber product having a filament denier of 0.75 to 3 or, perhaps, 5 and a uniform coating on the fibers of potassium salts of ethoxylated alkyl phosphate acid esters in the amount of from 0.2 to 1.0 %, based on the weight of the aramid fiber.

This invention also provides a process for making a fiber product comprising the steps of establishing an aqueous finish bath having 1 to 50% of potassium salts of ethoxylated alkyl phosphate acid esters based on the total weight of the bath, contacting the aqueous finish bath with aramid fiber having a denier of 0.75 to as much as 5, and drying the aramid fiber to leave a uniform coating of 0.2 to 1.0% potassium salts of ethoxylated alkyl phosphate acid esters on the fiber.

Detailed Description of the Invention

The fibers of this invention are aramid fibers and can be made from any aramid polymeric material. The aramid which is preferred is para-aramid and the preferred para-aramid is poly(p-phenylene terephthalamide). By "poly(p-phenylene terephthalamide)" (PPD-T) is meant the homopolymer resulting from equimolar polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other aromatic diamine with the p-phenylene diamine and of small amounts of other aromatic diacid chloride with the terephthaloyl chloride. As a general rule, in the make-up of PPD-T, other aromatic diamines and other aromatic diacid chlorides can, also, be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction. The fibers can be staple or continuous filaments of any denier.

Aramid fibers can, also, be made from meta-aramid and the preferred meta-aramid is poly(m-phenylene isophthalamide). Meta-aramids and meta-aramid fibers are disclosed in United States Patent No. 3,287,324. Para-aramids and para-aramid fibers are disclosed in United States Patents Nos. 3,869,429.

Aramid fibers are generally wet spun from spinning dope solutions of the aramid polymer and, after being extruded from a spinneret, the dope solution is coagulated in an aqueous coagulating bath either after passing through a non-coagulating gap or not. The coagulating step is followed by washing in various ways and drying, either under tension or not.

The finish of this invention is applied to the aramid fiber during the course of the fiber manufacture and is usually applied after the washing step. The finish is water soluble and can, therefore, be applied by conducting the fiber through an aqueous solution of the finish and then drying the fiber. It is possible to contact the aqueous finish bath with the aramid fiber while the fiber is still in the "never-dried" form. That is, before application of the finish, the fiber can still retain at least about 20 weight percent water from the spinning process. Applying the finish to never-dried fibers causes more of the finish to be imbibed into the fiber structure. While the benefit of the invention can be realized by adding the finish either to dried or to never-dried fibers, it is believed that finish which is somewhat bound to the fiber is more effective than finish which has been merely coated onto the outer surface of the fiber. It is, however, preferred and more practical to add the finish to dried fibers.

In preparation of yarns, many fibers are damaged by contact with fiber guides and other handling devices and yarns are sometimes misguided due to build up of static charges. Finishes provide means for lubricating fibers and dissipating static charge, thereby decreasing the fiber damage and improving fiber handling qualities. In the field of aramid yarn manufacture, the need for more effective finishes increases dramatically as processing speeds increase; and the need for more effective finishes is especially pronounced in aramid staple yarn manufacture.

Discrete staple fibers are manufactured into continuous spun yarn by means of the classic ring spinning method which can be summarized as sequentially comprising the steps of

(i) opening baled, compact, staple fiber by means of a "picker" machine, thereby forming loose clumps of staple fiber which are subsequently compressed into a loose batting called a "picker lap";

(ii) combing ("carding") the lap so that the discrete staple fibers are substantially parallelized and forming these parallelized staple fibers into a loose continuous strand called a "card sliver";

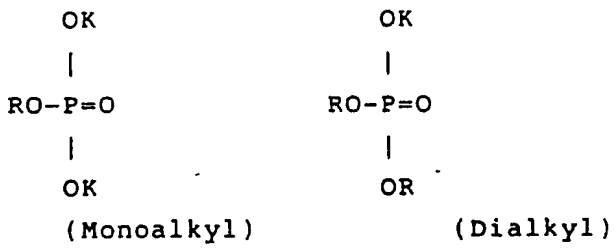
(iii) combining a plurality of card slivers into a single, more even strand called a "drawn sliver" in which the individual staple fibers are drawn into a more parallel relationship by means of a drawing frame;

(iv) further drawing one or several combined drawn sliver strands into a single continuous threadline, termed a "roving", with a minor amount of tensile strength by means of a "roving" machine which imparts twist to the threadline; and

(v) drawing and further twisting the roving on a ring spinning machine to produce a "spun yarn". Such a multi-step staple yarn manufacturing process results in excessive fiber damage which is evidenced by deposits on yarn contact surfaces, such as card clothing, draw rolls and spinning rolls. The buildup of deposits leads to further fiber damage, roll wraps and reduced productivity.

In further processing such as heat-treating, winding, and the like, fibers are conducted through and around various guide devices for yarn placement and alignment. This further processing, also, causes buildup of deposits from the fibers on the guide devices. This deposit buildup appears to be an especial problem with aramid fibers because the buildup of deposits is thought to be a function of the tension forces applied to the fibers and the resulting friction between the fibers and the guides. The present invention includes a finish which yields improved finish solution stability and improved fiber static properties and which does not result in deposit buildup on guide surfaces during manufacture of staple yarn or during additional handling before and after manufacture of the spun yarn.

The finish of this invention comprises a potassium salt of ethoxylated aliphatic phosphate acid esters, characterized as mono- or dialkyl phosphate acid esters. The aliphatic portion of the finish molecule is alkyl from 8 to 18 carbons with two or three ethylene oxide groups linked thereto. The structure of the finish molecule is as follows:



wherein R = $C_nH_{2n+1}(EO)_{1-3}$
EO is an ethylene oxide residue, and n = 8-18.

The finish compound of the present invention can be made by reacting aliphatic alcohol having 8-18 carbon atoms and 2 or 3 ethylene oxide groups with phosphorus pentoxide and then neutralizing the product with potassium hydroxide. The ethylene oxide groups increase water solubility of the finish and decrease the incidence of deposits.

As stated, the finishes of this invention are soluble in water to the extent of as much as 50% or, perhaps, more, based on weight of the water, and, in any event, finish material present in excess of the solubility limit is easily emulsified or dispersed. The finish of this invention is applied, most usually, by dipping the fibers into a finish bath made up as an aqueous solution of the finish compound. The concentration of finish in the finish bath should be such that, when all other aspects of the finish bath contact and finish bath drying are considered, the fiber product will have about 0.2 to 1.0% finish based on the weight of the starting aramid fiber. For most practice, it has been concluded that the finish bath should include from about 1 to 50% finish compound.

The finish of this invention is especially effective because it is water soluble and can, therefore, be applied from an aqueous solution. Application from a solution, permits application of an even coating of finish without rich or lean areas. The water solubility is not, however, the only quality which is necessary for obtaining a finish good for use with aramid fibers. It has been determined that several finishes with water solubility, when applied to aramid fibers, yield an aramid fiber product which has an even coating of finish and good static properties; but that those finishes, on aramid fibers, consistently leave a buildup of deposits when run across yarn contact surfaces. Examples of such water soluble finishes which leave excessive deposits on contact surfaces include: potassium salts of alkyl phosphate acid esters wherein the alkyl is 4-12 carbon atoms; potassium salts of ethoxylated alkyl amine sulfates such as tallow amine diethyl sulfate wherein the tallow includes from 2 to 20 ethylene oxide residues; diethyl amine salt of alkyl phosphate esters wherein the alkyl is a blend of 8, 10, and 12 carbon atoms; and potassium salt of alkyl phosphonate ethyl acid ester wherein the alkyl is 8 carbon atoms.

It should be noted that the finish used in the present invention incorporates elements of the materials listed above and, thereby, becomes a finish of excellent performance despite the poor performance of other materials having somewhat similar composition.

The present invention is based on the fact that aramid fibers having a finish material of particular potassium salts of ethoxylated aliphatic phosphate esters exhibit a combination of qualities which appear to be unique to that combination of fiber and finish.

Test Methods

Finish on yarn (FOY) is determined by dissolving the finish from a sample of yarn using methanol, evaporating the methanol to dryness, weighing the residue, weighing the clean yarn sample, and calculating the percent of finish based on the clean yarn.

$$\% \text{ FOY} = \frac{\text{weight of finish residue}}{\text{weight of clean yarn}} \times 100$$

Finish Uniformity is determined by microscopic inspection of the fibers in question. Separate splotches on lumps of finish denote "poor" finish uniformity. "Medium" finish uniformity indicates that the finish can

be detected microscopically as a substantially continuous but nonuniform coating. "Good" finish uniformity indicates that the finish can be detected microscopically as a continuous uniform coating. A finish of "Excellent" uniformity cannot be detected microscopically.

Finish Deposits are determined as the amount of finish material accumulated on a test fiber guide or yarn guide after passage of a known amount of fiber under specified conditions.

To conduct the test, the yarn in question is run at 100 yards per minute for about two minutes through two 14-rung tensional ladder guides under 1.5 grams per denier tension at a wrap angle of 180 degrees. After a known time, the finish deposits accumulated on the guide are removed and weighed and the total weight of yarn run through the guide is calculated. Finish deposits are reported as milligrams of deposits per kilogram of yarn run through the guide.

$$\text{Deposits (mg/kg)} = \frac{\text{grams deposits}}{\text{grams yarn}} \times 10^6$$

Description of the Preferred Embodiments

Example

In this example, fibers of this invention were prepared and were tested against fibers utilizing finishes outside the teaching of this invention.

Continuous yarns of dry PPD-T homopolymer fiber having filaments with a filament denier of 1.5 were conducted through a finish bath having a finish concentration of about 15 weight percent; the finish-soaked yarn was conducted through a crimper to crimp the yarn and to remove excess finish solution; additional finish was then added to the crimped yarn when required to achieve the desired finish on yarn; the yarn was cut into staple having a length of about 1 1/2 to 2 inches; and the staple was baled. Spun yarns were, subsequently, produced from the staple using the ring spinning method.

The staple was tested for finish content, finish uniformity, and finish deposits.

Finishes used in the tests and results from the tests of this example are shown in the Tables, below.

Table of Finishes

Run#	Identity
1	$C_{10}H_{21}(2EO)PO_4$ acid ester, Potassium salt
2	$C_{10}H_{21}(EO)PO_4$ acid ester, Potassium salt
3	$C_{12}H_{25}(2EO)PO_4$ acid ester, Potassium salt
4	$C_{8\text{-}10}(1.5EO)PO_4$ acid ester, Potassium salt
A	$[C_{12}N_{25}]_{1 \text{ and } 2}PO_4$ acid esters, Potassium salt
B	$C_4H_9PO_4$ acid ester, Potassium salt
C	$C_6H_{13}PO_4$ acid ester, Potassium salt
D	$C_8H_{17}PO_4$ acid ester, Potassium salt
E	Mixed C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}PO_4$ acid esters, K salt
F	Tallow Amine (2EO) Diethyl Sulfate, K salt
G	Tallow Amine (5EO) Diethyl Sulfate, K salt
H	Tallow Amine (10EO) Diethyl Sulfate, K salt
I	Tallow Amine (20EO) Diethyl Sulfate, K salt
J	C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}PO_4$ acid esters, DEA*
K	$C_8H_{17}C_2H_5PO_3$ (Phosphonate) acid ester, K salt

*DEA = Diethanol Amine

TABLE

Run#	Finish on Yarn	Finish Uniformity	Finish Deposits
1	0.39	Excellent	0
2	0.47	Excellent	0
3	0.20	Excellent	0
4	0.45	Excellent	0
A	0.30	Poor	heavy*
B	0.50	Excellent	heavy
C	0.50	Excellent	heavy
D	0.50	Excellent	heavy
E	0.50	Excellent	heavy
F	0.99	Excellent	19.3
G	1.01	Excellent	31.0
H	1.04	Excellent	37.0
I	0.88	Excellent	37.7
J	0.50	Excellent	heavy
K	0.50	Excellent	heavy

* "heavy" deposits means that the deposits were estimated to be greater than 10 mg/kg.

Claims

1. An aramid fiber having a filament denier of 0.75 to 5 and a uniform coating on the fiber of the potassium salt of an ethoxylated alkyl phosphate acid ester in an amount of from 0.2 to 1.0%, based on the weight of the aramid.
2. The aramid fiber of Claim 1 wherein the phosphate acid ester has at least one structure selected from the following structures:

wherein R = $C_nH_{2n+1}(EO)_{1-3}$,
EO is an ethylene oxide residue, and n = 8-18.
3. The aramid fiber of Claim 2 wherein R = $C_{10}H_{21}(EO)_2$.
4. The fiber of Claim 1 wherein the aramid is para-aramid.
5. The fiber of Claim 4 wherein the para-aramid is poly(p-phenylene terephthalamide).
6. The fiber of Claim 1 wherein the aramid is meta-aramid.
7. The fiber of Claim 6 wherein the meta-aramid is poly(m-phenylene isophthalamide).
8. A staple yarn of aramid fibers having a filament denier of 0.75 to 5 and a uniform coating on the fiber of the potassium salt of an ethoxylated alkyl phosphate acid ester in an amount of from 0.2 to 1.0%, based on the weight of the aramid.
9. The staple yarn of Claim 8 wherein the phosphate ester has at least one structure selected from the following structures:

wherein R = $C_nH_{2n+1}(EO)_{1-3}$,
EO is an ethylene oxide residue, and n = 8-18.

10. The staple yarn of Claim 9 wherein R = $C_{10}H_{21}(EO)_2$.

11. The staple yarn of Claim 8 wherein the aramid is para-aramid.

12. The staple yarn of Claim 11 wherein the para-aramid is poly(p-phenylene terephthalamide).

13. A process for making an aramid fiber product comprising the steps of:
a) establishing an aqueous bath having 1 to 50% of the potassium salt of an ethoxylated alkyl phosphate acid ester based on the weight of the water;
b) contacting the aqueous bath with aramid fiber having a denier of 0.75 to 5; and
c) drying the aramid fiber to leave a uniform coating of phosphate ester on the fiber in an amount of from 0.2 to 1.0% based on the weight of the aramid.

14. The process of Claim 13 wherein the aramid fiber is "never-dried", having more that 20 weight percent water in the fiber at the time of commencing the contacting step.

15. The process of Claim 13 wherein the phosphate ester has at least one structure selected from the following structures:

wherein R = $C_nH_{2n+1}(EO)_{1-3}$,
EO is an ethylene oxide residue, and n = 8-18.

16. The process of Claim 15 wherein R = $C_{10}H_{21}(EO)_2$.

17. The process of Claim 13 wherein the aramid is para-aramid.

18. The process of Claim 17 wherein the para-aramid is poly(p-phenylene terephthalamide).

Claims for the following Contracting State: ES

1. A process for making an aramid fiber product of an aramid fiber having a filament denier of 0.75 to 5 and a uniform coating on the fiber of the potassium salt of an ethoxylated alkyl phosphate acid ester in an amount of from 0.2 to 1.0%, based on the weight of the aramid comprising the steps of:
a) establishing an aqueous bath having 1 to 50% of the potassium salt of an ethoxylated alkyl phosphate acid ester based on the weight of the water;
b) contacting the aqueous bath with aramid fiber having a denier of 0.75 to 5; and
c) drying the aramid fiber to leave a uniform coating of phosphate ester on the fiber in an amount of from 0.2 to 1.0% based on the weight of the aramid.

2. The process of Claim 1 wherein the aramid fiber is "never-dried", having more that 20 weight percent water in the fiber at the time of commencing the contacting step.

3. The process of Claim 1 wherein the phosphate ester has at least one structure selected from the following structures:

wherein R = $C_nH_{2n+1}(EO)_{1-3}$,
EO is an ethylene oxide residue, and n = 8-18.

4. The process of Claim 3 wherein R = $C_{10}H_{21}(EO)_2$.

5. The process of Claim 1 wherein the aramid is para-aramid.

6. The process of Claim 5 wherein the para-aramid is poly(p-phenylene terephthalamide).

7. The process of claim 1 wherein the meta-aramid is poly(m-phenylene isophthalamide).

8. The process of claim 1 for making a staple yarn of aramid fibers having a filament denier of 0.75 to 5 and a uniform coating on the fiber of the potassium salt of an ethoxylated alkyl phosphate acid ester in an amount of from 0.2 to 1.0%, based on the weight of the aramid.

9. The process of claim 8 wherein the phosphate ester has at least one structure selected from the following structures:

wherein R = $C_nH_{2n+1}(EO)_{1-3}$,
EO is an ethylene oxide residue, and n = 8-18.

10. The process of claim 8 wherein the aramid is para-aramid.